

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### NO DRAWINGS

### Improvements in Xerographic Development

We, RANK-XEROX LIMITED, of Mortimer House, 37-41 Mortimer Street, London, W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—  
This invention relates to a process of electrographic development and composition thereof.

In the art of electrography it is known to develop an electrostatic pattern upon a surface by causing finely divided developer particles to be attracted thereto. Originally, triboelectrically charged dry particles were used exclusively, but it was subsequently found that in certain circumstances advantages could be obtained by suspending the particles in a dielectric liquid of suitable triboelectric characteristic.

Whether dry or liquid development is resorted to, the final image is made up of dry particles which must be made fast to the image bearing surface.

The object of the present invention is to provide an improved liquid development process and composition thereof.

The present invention provides an electrographic development process comprising the step of causing a surface bearing thereon an electrostatic pattern to come into contact with an emulsion including a dispersed phase of fine droplets of a developer liquid in a continuous phase of an electrically insulating carrier liquid substantially immiscible with said droplets, said droplets bearing an electrostatic charge of a polarity and magnitude inherently acquired by contact with said carrier liquid, whereby the droplets are attracted to and retained on said surface in the configuration of the pattern.

The invention also provides an electrographic developer composition comprising

an emulsion including a dispersed phase of fine droplets of a developer liquid in a continuous phase of an electrically insulating carrier liquid, the two liquids being such as to allow formation of fine droplets of the developer liquid dispersed in the carrier liquid and said droplets bearing an electrostatic charge of a polarity and magnitude inherently acquired by contact with said carrier liquid.

The developer liquid may be substantially non-volatile and coloured either by insoluble pigments or by dyes, such as crystal violet.

The carrier liquid may be volatile and preferably has a resistivity of at least  $10^9$ .

The developer liquid may be an aqueous dye solution.

The carrier liquid may be a hydrocarbon solvent, it may also be a silicone liquid.

The carrier liquid may contain minor quantities of a non-ionic emulsifier.

The invention will now be described by way of example only.

Generally a xerographic development process starts with an electrostatic latent image pattern on a suitable surface. The most common method of forming such an image involves depositing a uniform electrostatic charge on a xerographic plate including a photoconductive insulating layer and then selectively discharging the uniform charge by exposure of the plate to a pattern of light and shadow. Other methods are also known for forming electrostatic latent images on xerographic plates. Furthermore, methods are also known and are in use for forming charge patterns on insulating materials which do not have photoconductive patterns. In general, any electrostatic latent image, regardless of the method whereby it is formed, is a suitable starting point for development in accordance with the present invention.

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Xerographic plates fall generally into one of two classes. The first class of plate comprises a layer of vitreous photoconductive insulating material such as vitreous selenium or sulphur, which may optionally be coated on any suitable support material. The second class includes a photoconductive insulating layer comprising a dispersion of photoconductive particles, such as zinc oxide, in an insulating binder material such as resin. The photoconductive insulating layer may again be coated on a suitable support material. The first class of plate is characterized as having a photoconductive insulating layer which is substantially impermeable to liquids; whereas, the second class of plates have photoconductive insulating layers which physically resemble highly pigmented paints and accordingly tend to be slightly permeable or absorbent toward liquids. Both classes of plates are suitable for use with the present invention but the results achieved may be slightly different as will be further described hereinafter. Similarly, latent image bearing surfaces of the non-photoconductor type may be divided into impermeable and permeable types of materials. The first class is comprised of such things as insulating plastic films which may be self-supporting or coated on various supports such as paper or metal webs and the second class is comprised of permeable materials such as carefully dried paper. Again, these classes of latent image bearing materials are both usable with the methods of the present invention, although again with somewhat varying results.

In liquid development processes generally, development is accomplished by immersing or otherwise contacting the xerographic plate or other latent image bearing member with a liquid developer material comprising a suspension of finely divided developer material in a liquid carrier. The carrier liquid must be a highly insulating material with a volume resistivity of at least about  $10^{12}$  ohm centimeters in order to avoid discharge of the electrostatic latent image, and should not be a solvent for any part of the xerographic plate or other latent image bearing member. Additionally, it should not be so viscous as to prevent the motion of the developer material under the influence of electric fields and should usually be at least moderately volatile, since the desired result of the development process is a dry image. This is most readily achieved by allowing the carrier liquid to evaporate from the developed image leaving only the developer material behind. Many different liquids are suitable for use as carrier liquids in liquid development generally and more specifically in connection with the present invention. A particularly useful class of materials comprises refined petroleum hydrocarbons having a volatility at least about as great as that of kerosene

and preferably not more than about that of gasoline. Such materials are widely available and variously known as mineral spirits, petroleum naphtha and Stoddard solvent, and are also sold under such trade names as Solvesso (Esso Standard Oil Company) and Sovasol (Socony Mobil Oil Company). A particularly useful material of this class is Sohio Odorless Solvent (SOS) sold by the Standard Oil Company of Ohio. Other suitable hydrocarbon carrier liquids include aliphatic hydrocarbons starting with pentane; aromatic hydrocarbons such as benzene, toluene, and xylene; and alicyclic hydrocarbons such as cyclohexane or methycyclohexane. Halogenated hydrocarbons may also be used including carbon tetrachloride, trichloroethylene, brominated hydrocarbons such as bromobenzene, and fluorocarbons such as the higher boiling "Freon" (Registered Trade Mark) liquids. Suitable carrier liquids are not limited to volatile hydrocarbons and non-volatile non-hydrocarbon liquids such as silicone oils may be used. Dow Corning 200 (Registered Trade Mark) fluid is a particularly useful example of a silicone oil. Finally, the carrier liquid may be a normally solid material, such as a low melting wax which can be put into a liquid condition for the purposes of carrying out this invention. For general information on liquid development processes prior to the present invention, reference may be had to British Patent 755,486, U.S. Patent 2,899,335 and U.S. Patent 2,913,353.

In accordance with the present invention, the developer material used in connection with the liquid carrier is not a preground or predispersed solid material or even a precipitated solid material but is instead itself a liquid material which is substantially immiscible with the carrier liquid and is dispersed therein in the form of a suspension or emulsion of very small droplets. The developer material will also generally contain a dissolved dye or suspended pigment in order to render the developer material visible and therefore to make the developed images likewise visible. It may also contain dissolved resins, waxes or other normally solid materials which are in a liquified condition. Since the developer material is dispersed within the carrier liquid, it cannot discharge the electrostatic latent image until it deposits thereon and therefore the requirements for electrical resistivity of the developer material are much less stringent than for the carrier liquid. In the course of development, the developer material deposits on the electrostatic latent image in the form of discrete and mutually separated droplets or particles. As development proceeds, these droplets may coalesce to form a thin film which might, if conductive, tend to discharge the latent image. At this point, however, the latent image is

already substantially developed, and furthermore, a thin film is much less effective in discharging a surface than is a bulk mass of material such as the carrier liquid. For these reasons, the developer material may have a resistivity many orders of magnitude less than that of the carrier liquid which preferably have a resistivity of at least  $10^9$  ohm-centimeters. Regardless of the validity of this theoretical explanation it has been found, contrary to all previous expectations, that the developer liquid may actually be as electrically conductive as water or even as conductive as an aqueous solution of copper sulphate. Suitable materials thus include water and aqueous solutions generally; monohydric alcohols, particularly amyl alcohol, polyhydric alcohols such as ethylene glycol, propylene glycol, glycerol; ketones such as acetone, methylethyl ketone, diethylketone; aldehydes such as acetaldehyde and esters such as ethyl acetate, methyl propionate and ethyl acetoacetate.

An almost limitless number of combinations of other carrier liquids and developer materials can be selected from any chemical handbook and which meet the above-mentioned general requirements. A combination which has been found particularly suitable comprises the above-mentioned Sohio Odorless Solvent as a carrier liquid and ethylene glycol as the developer material. The glycol can be coloured by dissolving 5% by weight of a dye such as crystal violet or malachite green. Several methods may be used to form an emulsion of the ethylene glycol and the carrier liquid. One method is to form a concentrated solution of the dyed ethylene glycol in alcohol and then to dilute this mixture with a large quantity of the carrier liquid to 0.1% by weight glycol concentration whereupon the ethylene glycol separates out in the form of fine droplets. Another method involves utilization of the fact that the ethylene glycol, while normally insoluble in the carrier liquid, becomes soluble at high temperatures. Accordingly, 0.1% by weight ethylene glycol may be dissolved in the hot petroleum solvent which is then allowed to cool, again precipitating the ethylene glycol in the form of fine droplets. It is also possible to form a suspension by purely mechanical means such as using a domestic homogenizer such as a Waring Blendor made by Winsted Hardware Manufacturing Company, Winsted, Connecticut or an Osterizer made by the John Oster Manufacturing Company, Racine, Wisconsin.

Emulsions formed by the above methods tend to be quite unstable and must be used immediately after they are formed. It is, however, a simple matter to re-emulsify these materials when they settle out. It is also rather difficult to produce very fine droplet

sizes in such emulsions. Much more stable and finer grain emulsions may be prepared through the addition of certain surface active agents to the carrier liquid. In addition to having suitable emulsifying properties, the surface active agent should not significantly decrease the electrical resistivity of the carrier liquid. Certain non-ionic sorbitan fatty acid esters have been found particularly suitable as emulsifiers. For instance, the addition of 0.1% by weight of Span 85 (a sorbitan fatty acid ester manufactured by Atlas Powder Company, Wilmington, Delaware) to Sohio Odorless Solvent permits the preparation with a homogenizer of a 0.1% by weight ethylene glycol emulsion which remains usable for several hours with only occasional agitation and which forms dense developed images composed of microscopic droplets. Other types of surface active agents produce similar results. For example, a developer can be formed by mixing 12 drops of Sotex 3CV surfactant (an ester type surfactant made by Synthetic Chemicals, Inc.), 5 drops of ethanol and 2 drops of a saturated ethanol solution of alphanurine dye and then homogenizing the mixture with 20 cubic centimeters of petroleum ether, forming a quite stable emulsion. As a further example, an emulsion may be formed by mixing 0.6 cubic centimeters of a 1% by weight aqueous solution of crystal violet dye with 100 cubic centimeters of Sohio Odorless Solvent. Addition of 0.1 cubic centimeter or less of Tergetol NP27 (Registered Trade Mark), a non-ionic surfactant made by Union Carbide Chemical Company, enhances the stability of the emulsion without affecting its ability to develop an image. Somewhat higher concentrations of these surface active agents can be tolerated without impairing image quality. However, it has not thus far been found wholly desirable to increase the concentration of surface active agent to the point that mechanical homogenization can be dispensed with because the emulsions so formed produce relatively weak images. It is not presently known whether this is due to the extremely small size of droplets so formed or to the higher conductivity produced in the carrier liquid by these surface active agents. Certain developer emulsions are quite stable without the addition of surfactants or emulsifiers. Thus, emulsions of aqueous materials in Dow Corning 200 silicone fluid retain their xerographic developing properties for several hours without agitation.

It has been found to be characteristic of these liquid-in-liquid emulsions that the dispersed phase acquires an electrostatic charge with respect to the carrier liquid, and this charge is desirable in promoting the attraction of the droplets toward the electrostatic latent image. Such inherent droplet charging takes place with the above-described ethylene

glycol-petroleum solvent emulsion in which the droplets acquire a positive charge, and this emulsion is accordingly effective as a xerographic developer. To use this or other emulsions for the development of a xerographic plate, it is only necessary to immerse a plate in a container of the emulsion or else to pour the emulsion over the plate or otherwise contact the plate with the emulsion. The dispersed droplets are selectively electrostatically attracted toward the latent image and deposit thereon in image configuration. This deposition is generally complete within a few seconds at most. Where the xerographic plate or other latent image bearing member is of the permeable type previously described, the developer material is not only attracted to the plate, but is absorbed within the plate within a few seconds to form a completely permanent image which needs no further fixing operation to be rendered permanent. If the xerographic plate is of the impermeable type, the developed image will remain on the plate surface rather than soaking in. This will lead to the formation of a dry and moderately adherent image if the developer material is itself volatile. If, however, a non-volatile material such as ethylene glycol is employed, the image will remain in the liquid condition. If the xerographic plate is pressed against a sheet of paper or other permeable transfer material while the developer material is still liquid, the developer material will transfer from the impermeable plate to the permeable transfer material and soak into the transfer material forming an inherently permanent image thereon. This may be done either before or after the carrier liquid, if volatile, has evaporated. It has been found that image transfer is generally improved by using conventional electrostatic transfer techniques to supplement transfer by diffusion or soaking. In accordance with conventional electrostatic transfer techniques an electrostatic charge is placed on the back surface of the paper or other transfer material while it is in contact with the xerographic plate. The electrostatic charge may be applied by a corona device or an electrically conductive roller. Transfer may generally be effected even after a volatile developer has evaporated by contacting the xerographic plate with a suitably moistened sheet of paper. Again, the need for a separate fixing operation or special transfer material has been eliminated and the xerographic plate can be washed free of any remaining developer material and be reused.

In accordance with the present invention it becomes possible for the first time to use ordinary aqueous inks as xerographic developers. Thus for example washable blue "Scrip" (Registered Trade Mark) writing fluid (W. A. Sheaffer Pen Co., Fort Madison, Iowa) which is believed to be an aqueous

solution of various dyes, may be emulsified in petroleum solvent and used to develop a xerographic image. Such an ink image is self fixing on a permeable xerographic plate or may be transferred from a selenium xerographic plate to a sheet of paper on which it is again self fixing. The same procedures and results may be had with India ink, which is an aqueous suspension of fine carbon black particles, rather than an aqueous dye solution. Accordingly, the dispersed material according to the present invention may comprise droplets which in turn contain dispersed solid particles, as well as droplets which do not contain solid particles. Such material is also intended to be covered by the term "liquid" as used in the specification and claims. Many of the pigment suspensions used as liquid developers in the prior art may be used as the dispersed phase of the present invention, but it now becomes possible to use aqueous pigment suspensions which were previously not usable as xerographic developers because of their electrical conductivity.

While the invention has not hitherto been described in terms of specific forms of developing apparatus, it will be apparent to those skilled in the art that it is adaptable to various forms of apparatus including automatic apparatus and is likewise adaptable for use with xerographic plates of various physical forms including, for example, flexible webs and rotating cylindrical drums. These and various other embodiments and modifications lie within the scope of the invention and are intended to be encompassed by the appended claims.

#### WHAT WE CLAIM IS:—

1. An electrographic development process comprising the step of causing a surface bearing thereon an electrostatic pattern to come into contact with an emulsion including a dispersed phase of fine droplets of a developer liquid in a continuous phase of an electrically insulating carrier liquid substantially immiscible with said droplets, said droplets bearing an electrostatic charge of a polarity and magnitude inherently acquired by contact with said carrier liquid, whereby the droplets are attracted to and retained on said surface in the configuration of the pattern.

2. An electrographic process according to claim 1, wherein said surface is at least slightly permeable, whereby the droplets are attracted to and at least partly absorbed into said surface in the configuration of said pattern.

3. An electrographic process according to claim 1, wherein said surface is substantially impermeable and an at least slightly permeable transfer surface is caused to come into and out of contact with said impermeable surface when the droplets of said developer liquid have been attracted thereto

and retained thereon.

4. A process as claimed in Claim 3, wherein the transfer surface is subjected to an electrostatic field suitable to assist transfer from the impermeable surface.
5. A process as claimed in any one of preceding claims, wherein the carrier liquid has a resistivity of at least  $10^{12}$  ohm-cm.
6. A process as claimed in any one of preceding claims, wherein the developer liquid is coloured.
7. A process as claimed in any one of preceding claims, wherein the carrier liquid is volatile and the developer liquid is relatively non-volatile.
8. A process as claimed in any one of preceding claims, wherein the developer liquid is coloured by insoluble pigment particles.
9. A process as claimed in any one of Claims 1 to 7, wherein the developer liquid is coloured by a dye.
10. A process as claimed in Claim 9, wherein said dye is crystal violet.
11. A process as claimed in any one of claims 1 to 7, wherein the developer liquid is an aqueous dye solution.
12. A process as claimed in any one of preceding claims, wherein the carrier liquid is a refined petroleum hydrocarbon.
13. A process as claimed in Claim 6, wherein the carrier liquid is a refined petroleum hydrocarbon solvent and the developer liquid is dyed ethylene glycol.
14. A process as claimed in any one of preceding claims, wherein the carrier liquid contains a non-ionic emulsifier in such an amount as to increase the stability of the emulsion without impairing its ability to develop an image.
15. A process as claimed in Claim 13, wherein the carrier liquid contains 0.1% by weight of sorbitan fatty acid ester emulsifier and the developer liquid is a dyed ethylene glycol.
16. A process as claimed in any one of Claims 1 to 11, wherein the carrier liquid is a silicone liquid.
17. An electrographic developer composition comprising an emulsion including a dispersed phase of fine droplets of a developer liquid in a continuous phase of an electrically insulating carrier liquid, the two liquids being such as to allow formation of fine droplets of the developer liquid dispersed in the carrier liquid and said droplets bearing an electrostatic charge of a polarity and magnitude inherently acquired by contact with said carrier liquid.
18. A composition as claimed in Claim 60 17, wherein the carrier liquid has a resistivity of at least  $10^{12}$  ohm-cm.
19. A composition as claimed in Claim 17 or in Claim 18, wherein the developer liquid is coloured.
20. A composition as claimed in any one of Claims 17 to 19, wherein the carrier liquid is volatile and the developer liquid is relatively non-volatile.
21. A composition as claimed in any one of Claims 17 to 20, wherein the developer liquid is coloured by insoluble pigment particles.
22. A composition as claimed in any one of Claims 17 to 20, wherein the developer liquid is coloured by a dye.
23. A composition as claimed in Claim 22, wherein said dye is crystal violet.
24. A composition as claimed in any one of Claims 17 to 20, wherein the developer liquid is an aqueous dye solution.
25. A composition as claimed in any one of Claims 17 to 23, wherein the carrier liquid is a refined petroleum hydrocarbon.
26. A composition as claimed in Claim 19, wherein the carrier liquid is a refined petroleum hydrocarbon solvent and the developer liquid is dyed ethylene glycol.
27. A composition as claimed in any one of Claims 17 to 26, wherein the carrier liquid contains a non-ionic emulsifier in such an amount as to increase the stability of the emulsion without impairing its ability to develop an image.
28. A composition as claimed in Claim 26, wherein the carrier liquid contains 0.1% by weight sorbitan fatty acid ester emulsifier and the developer liquid is dyed ethylene glycol.
29. A composition as claimed in any one of Claims 17 to 24, wherein the carrier liquid is a silicone.
30. An electrographic print when developed according to the electrographic development method as claimed in any one of Claims 1 to 16.
31. An electrographic print when developed with the electrographic developer composition as claimed in any one of Claims 17 to 29.
32. An electrographic development process according to claim 1 substantially as described.
33. An electrographic developer composition according to claim 17 substantially as described.

A. POOLE,  
Acting for Applicants.